

for medical use), as dermal gels in EP 0095892 (wound-covering materials), for use as cooling medium in EP 0070986 (gel for use as cooling-medium), as insulation gel for low temperatures in JP 57190072, as phantoms for NMR diagnosis in GB 2209401 (phantoms for NMR diagnosis) or as golf ball filling in GB 2182571 (golf ball cores).

A further modified method is described in US 6231605 wherein, starting from an aqueous PVA solution, e.g. in example 1 with  $C_p = 15\%$  three freeze/thaw cycles were first applied at  $-20^{\circ}\text{C}$  whereafter the gel obtained was placed in water and thus swollen. The gel was transparent in this state but so weak that it could not maintain its shape outside water. The swollen gel was then subjected to another two freeze/thaw treatments and an opaque elastic gel having a modulus of elasticity of around 0.4 MPa was then obtained. Such gels were also proposed for use as tissue replacement in the human body, e.g. for heart valves, vessels, tendons, cartilage, urethral meniscus.

In a further modified method in US 4663358 the PVA solution is prepared using mixtures of water and organic solvents, especially DMSO and then frozen at  $-20^{\circ}\text{C}$ . The gel obtained is then stored in water to extract most of the DMSO, dried in the atmosphere and then under vacuum to extract the remainder of the DMSO. After swelling the samples in water, PVAG was obtained which had a transparency of up to 99% and strengths of up to 5.6 MPa. Such transparent PVAG was proposed for applications in the field of biomedicine and for the food industry.

JP 48-030462 discloses a method for manufacturing polyvinyl alcohol gels where a type of polyvinyl alcohol or a polyvinyl alcohol derivative is mixed with water and added to strengthen plastic fibres (e.g. Rayon or Vynylon). The PVA thus obtained is a composite of PVA and plastic fibres. In this method cold treatment also takes place at -30°C or at -40°C for 24 hours.

JP-5245138 describes a method for manufacturing a PVAG likewise using only one type of PVA which is initially dissolved in an at least partly polar solvent, the solution is cooled to room temperature and is finally brought into a medium which has only a weakly or non-dissolving action for PVA. An aqueous soft gel used as an ultrasound medium is obtained by this method.

JP-711327 describes a method for manufacturing a thin sheet for transfer printing. The film material consists of a first PVA resin with a very high average DP of at least 3200 and a second PVA resin having an average DP of less than 3200. Both PVA resins have a degree of saponification or degree of hydrolysis DH of 65-95 mole %. No softener is mentioned. It is questionable whether a gel is formed at all here. The film obtained by this method has a short swelling time or softening time when it floats on the surface of water.

US-4542013 discloses a polymer diffusion matrix and a method for its manufacture. This matrix material contains a first PVA component with a molecular weight in the range of

about 5000 to about 40,000 and a second PVA component with a molecular weight in the range of about 90,000 to about 150,000, which corresponds to DP ranges of 114 to 909 or 2045 to 3409, respectively.

As has been mentioned, said methods for manufacturing biocompatible PVAG have the common feature that they start from a pourable solution and at least one freeze/thaw cycle is applied. It is known to the person skilled in the art that the mechanical properties of the PVAG obtained in the various versions of the method increase with the concentration  $C_p$  of the PVA used in the solution, with increasing degree of polymerisation DP and with increasing degree of hydrolysis. In this method, however, the parameters  $C_p$  and DP cannot be optimised independently of one another since advantageous higher degrees of polymerisation DP cause the viscosity of the solution to increase substantially so that it becomes difficult to manufacture a solution and it is no longer pourable. Maximum solution viscosities lie in the range of 10,000 mPa. For example, Mowiol 66-100, one of the highest-molecular commercially available PVAs with a degree of hydrolysis DH of 99.4% and a degree of polymerisation DP of around 4,500 already has the maximum processable viscosity of 10,000 mPa at a concentration  $C_p$  of 10% at room temperature, at 80°C the limiting concentration  $C_p$  is around 15%. In the case of higher-molecular PVA, the limiting concentration is even lower. This is an important disadvantage of the conventional methods. A further disadvantage is the long time required by the conventional

methods, a single freeze/thaw cycle for example lasts at least 24 h, dehydration by lyophilisation takes about 10 h, the removal of organic solvents takes days. On the whole it is desirable to be able to process higher concentrations  $C_p$ , to develop simpler and shorter methods, to improve the mechanical properties of PVAG (higher strengths and moduli of elasticity) and to achieve transparency even in pure PVA water systems without the assistance of organic solvents